Bismuth-Catalyzed Allylation of para-Quinone Methides

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Table of Contents
1. General information..................................................................................................................3
2. The synthesis of para-quinone methides (p-QMs).................................................................4
3. General experimental 1,6-addition reaction procedure .........................................................5
4. The transformation of the products .........................................................................................6
5. Analytical data of all compounds..........................................................................................10
6. NMR copies of all compounds..............................................................................................23
7. X-ray crystallography data of 6n...........................................................................................58
8. Reference..................................................................................................................................60
1. General information: Commercial reagents were used as received, unless otherwise stated. \(^1\)H and \(^{13}\)C NMR were recorded on 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). Mass spectra were obtained using electrospray ionization (ESI) mass spectrometer.
2. The synthesis of \textit{para}-quinone methides (\textit{p}-QMs)

The \textit{para}-quinone methides (\textit{p}-QMs) $1a-1s^{la}$, $1w-1y^{la}$, $1t^{lc}$, $1u^{lb}$, $1v^{lc}$ were prepared according to the reported literature procedures.
3. General experimental 1,6-addition reaction procedure

3.1 1,6-addition of \( p \)-QMs

\[
\begin{align*}
\text{R}_1 \text{C=CH}_2 + \text{O} & \rightarrow \text{R}_1 \text{C=CH}_2 \text{O} \\
\text{R}_1 & \text{C=CH}_2 \text{O} \quad \text{Bi(OTf)}_3 (0.5\text{~5 mol%}) \\
\text{R}_1 & \text{C=CH}_2 \text{O} \quad 1,4\text{-dioxane, rt} \\
\text{R}_1 & \text{C=CH}_2 \text{O} \quad \text{R}_1 \text{C=CH}_2 \text{O} \\
\end{align*}
\]

To a stirred solution of cyclohexa-2,5-dien-1-one 1 (0.05 mmol) and allylboronic acid pinacol ester 2 (0.1 mmol) in dry 1,4-dioxane (0.5 mL) at room temperature were added Bi(OTf)_3. The reactions were monitored by TLC. After 1 were consumed completely, the reaction solution were concentrated in vacuo and the crude products were purified by flash chromatography eluting with (petroleum ether/ethyl acetate 30:1) to afford the products 3.

3.2 The synthesis of 3z

\[
\begin{align*}
\text{t-Bu} & \text{t-Bu} + \text{CH}_2\text{Cl}_2, \text{rt}, 24\text{h} \\
\text{t-Bu} & \text{t-Bu} \quad \text{Bi(OTf)}_3 (10\text{ mol%}) \\
\text{t-Bu} & \text{t-Bu} \quad \text{CH}_2\text{Cl}_2, \text{rt}, 24\text{h} \\
\text{t-Bu} & \text{t-Bu} \quad \text{3z 87\% yield} \\
\end{align*}
\]

To a stirred solution of 4-(4-(benzyloxy)benzylidene)-2,6-di-tert-butylocyclohexa-2,5-dien-1-one 1k (0.05 mmol) and beta-styryltrifluoroboric acid potassium 2z (0.1 mmol) in dry CH_2Cl_2 (0.5 mL) at room temperature was added Bi(OTf)_3. The reaction was monitored by TLC. After 1k was consumed completely, the reaction solution was concentrated in vacuo and the crude product was purified by flash chromatography eluting with (petroleum ether/ethyl acetate 30:1) to afford the product 3z.
4. The transformation of the products
4.1 The transformation of 3o

The synthesis of 4o
Under Ar atmosphere, to a stirred solution of 3o (450 mg, 1.2 mmol) in 10.0 mL anhydrous toluene was added 10:1 Tf2O/TfOH (10:1 v/v) 400 μL dropwise. The resulting mixture was stirred for 5h at room temperature. Then 10 mL H2O was added to quenched the reaction and extracted with ethyl acetate. The organic phase was dried over Na2SO4 and concentrated under reduced pressure. The crude residue was purified with silica gel by column chromatography (petroleum ether/ethyl acetate 10/1) to afford 4o 301 mg as a colorless oil in 80 % yield.

The synthesis of 5o
A mixture of 4o (251mg, 0.8 mmol) and Nafion-H (200 wt %) in toluene (5 mL) was refluxed 3 h until completion of the reaction. The solid resinsulfonic acid was then filtered off and the solvent was concentrated under reduced pressure. The crude residue was purified with silica gel by column chromatography (petroleum ether/ethyl acetate 3/1) to afford 5o 134 mg as a colorless oil in 52 % yield.

The synthesis of 6o
Under Ar atmosphere, 5o (129 mg, 0.5 mmol) was added to a solution of Grubbs II catalyst (5 mol %) in 5ml CH2Cl2. The resulting mixture was heated to reflux for 3h. The solvent was concentrated under reduced pressure. Then the crude residue was purified with silica gel by column chromatography (petroleum ether /ethyl acetate 2/1) to afford 6o 92 mg as a white solid in 75 % yield.
4.2 The transformation of 3e

m-CPBA (77.6mg, 1.5 equiv) was added to a solution of 3e (111.3, 0.3 mmol) in CH$_2$Cl$_2$ (5mL) at 0 °C. The resulting solution was stirred at room temperature for 24 h. Next, the reaction mixture was cooled to 0 °C and quenched with saturated NaHCO$_3$ (10 mL). The organic layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$. The organic layer was separated, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The crude residue was purified with silica gel by column chromatography (petroleum ether /ethyl acetate 50/1) to afford 7e 110 mg as a white solid in 95 % yield.
4.3 The transformation of 3n

![Chemical structure of 3n, 4n, 5n, 6n, 7n, and 8n]

**The synthesis of 4n**

BH$_3$•THF (1.0 M solution in THF, 1.16 mmol) was added to a solution of 3n (430 mg, 1.16 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 10 min at 0 °C and for 1 h at room temperature. 15% NaOH (aq) (1.5 eq) and 30% H$_2$O$_2$ (aq) (2.0 eq) were successively added at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated NaCl (aq) and the mixture was extracted with Et$_2$O. The organic layer was dried over MgSO$_4$, filtered, and concentrated under vacuum. The crude residue was purified with silica gel by column chromatography (petroleum ether/ethyl acetate 5/1) to afford 4n 395 mg as a white oil in 88% yield.

**The synthesis of 5n**

To a stirred solution of 4n (375 mg, 0.96 mmol) in CH$_2$Cl$_2$ (10.0 mL) was added NaHCO$_3$ (1.2 g, 14.5 mmol) and Dess-Martin periodinane (1.0 g, 2.4 mmol). The resulting slurry was stirred at room temperature for 3 h before filtrated through celite and concentrated under reduced pressure. The crude residue was purified with silica gel by column chromatography (petroleum ether/ethyl acetate 20/1) to afford 5n 360 mg as a white oil in 97% yield.

**The synthesis of 6n**

To a stirred solution of 5n (136 mg, 0.35 mmol) at 0°C in acetone (5 mL) was added Jones reagent (CrO$_3$/H$_2$SO$_4$ = 1 mmol/4 mL, 0.08 mol). The solution was stirred at room temperature for 2 h and quenched with iPrOH. The reaction was quenched with H$_2$O and the mixture was extracted with ethyl acetate, and concentrated under reduced pressure. The crude residue was purified with silica gel by column chromatography (petroleum ether/ethyl acetate 3/1) to afford 6n 107 mg as a white solid in 76% yield.

**The synthesis of 7n**

To a stirred solution of 5n (98 mg, 0.25 mmol) in EtOH (3 mL) was added hydroxyamine hydrochloride (52 mg, 0.75 mmol) and pyridine (0.04 mL). The resulting mixture was heated to reflux for 1 h. The solvent was concentrated under reduced pressure, EtOAc (5 mL) and water (5
mL) were added, the organic layer was washed with 5% HCl and concentrated under reduced pressure. Then the crude residue was purified with silica gel by column chromatography (petroleum ether /ethyl acetate 5/1) to afford 78 80 mg as a white oil in 80 % yield.

The synthesis of 8n

To a stirred solution of 1-(2,4-dinitrophenyl)hydrazine (55mg, 0.28 mmol) and concentrated sulfuric acid (40 uL) in MeOH (3mL) at 50 °C was added a solution of 5n (98mg, 0.25 mmol) in MeOH(2 mL). The resulting reaction mixture was stirred at 50 °C for additional 1h. Then the reaction mixture was concentrated to 1/4 of its original volume under vacuo and diluted with water (5 mL). The precipitates were separated by filtration and washed with 3% aqueous NaHCO₃ (3 × 1 mL) and water (3 × 1 mL). Products were recrystallized from EtOH to give 8n 128mg as a yellow solid in 90 % yield.
5. Analytical data of all compounds

**Compound 3a:** 2,6-di-tert-butyl-4-(1-phenylbut-3-en-1-yl)phenol.

![Diagram of Compound 3a]

**Compound 3a:** colorless oil, 99% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 – 7.21 (m, 3H), 7.16 (d, $J = 8.4$ Hz, 2H), 6.99 (s, 2H), 5.75 – 5.62 (m, 1H), 5.06 (s, 1H), 5.04 – 4.92 (m, 2H), 3.89 (t, $J = 7.9$ Hz, 1H), 2.79 – 2.70 (m, 2H), 1.40 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.11, 145.15, 137.52, 135.63, 135.25, 128.42, 128.14, 126.07, 124.45, 116.03, 51.45, 40.82, 34.51, 30.49.

HRMS (ESI) caleld for C$_{24}$H$_{32}$O (M+NH$_4$)$^+$: 354.2791, found: 354.2794.

**Compound 3b:** 2,6-di-tert-butyl-4-(1-(2-methoxyphenyl)but-3-en-1-yl)phenol.

![Diagram of Compound 3b]

**Compound 3b:** colorless oil, 99% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 – 7.07 (m, 4H), 6.94 – 6.81 (m, 2H), 5.81 – 5.65 (m, 1H), 5.07 – 4.85 (m, 3H), 4.42 (t, $J = 7.9$ Hz, 1H), 3.80 (s, 3H), 2.77 (dt, $J = 14.8, 7.7$ Hz, 2H), 1.40 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.07, 151.88, 137.92, 135.26, 134.93, 133.69, 128.08, 126.90, 124.82, 120.58, 115.60, 110.76, 55.55, 43.19, 39.58, 34.48, 30.52.

HRMS (ESI) caleld for C$_{25}$H$_{34}$O$_2$ (M+NH$_4$)$^+$: 384.2897, found: 384.2899.

**Compound 3c:** 2,6-di-tert-butyl-4-(1-(o-tolyl)but-3-en-1-yl)phenol.

![Diagram of Compound 3c]

**Compound 3c:** colorless oil, 99% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28 (d, $J = 7.7$ Hz, 1H), 7.21 – 7.05 (m, 3H), 6.98 (s, 2H), 5.79 – 5.65 (m, 1H), 5.06 – 4.88 (m, 2H), 4.12 (t, $J = 7.7$ Hz, 1H), 2.75 (d, $J = 5.8$ Hz, 2H), 2.31 (s, 3H), 1.38 (s, 18H).
\[ C\text{ NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta 151.96, 143.03, 137.59, 136.18, 135.79, 134.79, 130.48, 126.89, 126.04, 125.87, 124.70, 115.94, 46.65, 40.85, 34.47, 30.48, 20.21. \]

HRMS (ESI) caleed for C\text{25}H\text{34}O (M-H): 349.2537, found: 349.2543.

**Compound 3d**: 2,6-di-tert-butyl-4-(1-(2-chlorophenyl)but-3-en-1-yl)phenol.

**Compound 3d**: colorless oil, 99% isolated yield.

\[ \text{\textsuperscript{1}H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta 7.33 \ (d, J = 8.0 \text{ Hz, 1H}), 7.28 \ (s, 1H), 7.23 - 7.17 \ (m, 1H), 7.10 \ (d, J = 7.8 \text{ Hz, 1H}), 7.07 \ (s, 2H), 5.81 - 5.63 \ (m, 1H), 5.10 - 4.89 \ (m, 3H), 4.53 \ (t, J = 7.9 \text{ Hz, 1H}), 2.78 \ (t, J = 7.0 \text{ Hz, 2H}), 1.40 \ (s, 18H). \]

\[ \text{\textsuperscript{13}C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta 142.63, 136.91, 135.60, 133.70, 129.70, 128.78, 127.17, 126.92, 124.76, 116.34, 46.34, 39.87, 34.50, 30.48. \]

HRMS (ESI) caleed for C\text{24}H\text{31}ClO (M+NH\textsubscript{4})\textsuperscript{+}: 388.2402, found: 388.2393.

**Compound 3e**: 4-(1-(2-bromophenyl)but-3-en-1-yl)-2,6-di-tert-butylphenol.

**Compound 3e**: colorless oil, 96% isolated yield.

\[ \text{\textsuperscript{1}H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta 7.53 \ (d, J = 7.4 \text{ Hz, 1H}), 7.24 \ (d, J = 3.2 \text{ Hz, 2H}), 7.09 \ (s, 2H), 7.02 \ (dd, J = 8.4, 2.7 \text{ Hz, 1H}), 5.81 - 5.64 \ (m, 1H), 5.12 - 4.91 \ (m, 3H), 4.52 \ (t, J = 7.8 \text{ Hz, 1H}), 2.77 \ (dd, J = 8.6, 5.8 \text{ Hz, 2H}), 1.40 \ (s, 18H). \]

\[ \text{\textsuperscript{13}C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta 152.24, 144.31, 136.83, 135.60, 133.68, 133.02, 128.97, 127.59, 127.52, 125.27, 124.78, 116.39, 48.92, 40.03, 34.52, 30.49. \]

HRMS (ESI) caleed for C\text{24}H\text{31}BrO (M-H): 413.1486, found: 413.1477.

**Compound 3f**: 2,6-di-tert-butyl-4-(1-(3-methoxyphenyl)but-3-en-1-yl)phenol.

**Compound 3f**: colorless oil, 99% isolated yield.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.19 (d, $J = 7.9$ Hz, 1H), 7.04 (s, 2H), 6.90 – 6.69 (m, 3H), 5.80 – 5.65 (m, 1H), 5.09 – 4.89 (m, 3H), 3.88 (t, $J = 7.9$ Hz, 1H), 3.78 (s, 3H), 2.77 (dd, $J = 11.4$, 6.9 Hz, 2H), 1.41 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.62, 152.15, 146.85, 137.47, 135.60, 135.04, 129.34, 124.40, 120.56, 116.05, 114.19, 111.05, 55.25, 51.49, 40.77, 34.50, 30.48.

HRMS (ESI) cale for C$_{25}$H$_{34}$O$_2$(M+NH$_4$)$^+$: 384.2897, found: 384.2894.

**Compound 3g:** 2,6-di-tert-butyl-4-(1-(m-tolyl)but-3-en-1-yl)phenol.

\[
\begin{array}{c}
\text{Ph} \\
\text{t-Bu} \\
\text{t-Bu} \\
\text{OH} \\
\text{Me} \\
\end{array}
\]

**Compound 3g:** colorless oil, 97% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.17 (t, $J = 7.8$ Hz, 1H), 7.09 – 6.95 (m, 5H), 5.78 – 5.64 (m, 1H), 5.08 – 4.89 (m, 3H), 3.86 (t, $J = 7.9$ Hz, 1H), 2.83 – 2.70 (m, 2H), 2.31 (s, 3H), 1.40 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.08, 145.01, 137.87, 137.62, 135.55, 135.34, 129.05, 128.29, 126.85, 124.94, 124.42, 115.93, 51.48, 40.87, 34.50, 30.48, 21.71.

HRMS (ESI) cale for C$_{25}$H$_{34}$O (M-H)$^-$: 368.2948, found: 368.2949.

**Compound 3h:** 2,6-di-tert-butyl-4-(1-(3-chlorophenyl)but-3-en-1-yl)phenol.

\[
\begin{array}{c}
\text{Ph} \\
\text{t-Bu} \\
\text{t-Bu} \\
\text{Cl} \\
\text{OH} \\
\end{array}
\]

**Compound 3h:** colorless oil, 99% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.18 (m, 2H), 7.17 – 7.10 (m, 2H), 7.00 (s, 2H), 5.77 – 5.59 (m, 1H), 5.07 (s, 1H), 5.06 – 4.92 (m, 2H), 3.88 (t, $J = 7.8$ Hz, 1H), 2.81 – 2.69 (m, 2H), 1.41 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.31, 147.24, 136.94, 135.78, 134.44, 134.15, 129.67, 128.37, 126.28, 124.37, 116.46, 51.13, 40.56, 34.52, 30.45.


**Compound 3i:** 4-(1-(3-bromophenyl)but-3-en-1-yl)-2,6-di-tert-butylphenol.

\[
\begin{array}{c}
\text{Ph} \\
\text{Br} \\
\text{OH} \\
\text{t-Bu} \\
\text{t-Bu} \\
\end{array}
\]

**Compound 3i:** colorless oil, 82% isolated yield.
\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \delta \ 7.38 \ (s, 1H), \ 7.33 - 7.25 \ (m, 2H), \ 7.15 \ (d, J = 7.0 \text{ Hz, } 2H), \ 6.99 \ (s, 2H), \ 5.75 - 5.60 \ (m, 1H), \ 5.07 \ (s, 1H), \ 5.06 - 4.92 \ (m, 2H), \ 3.87 \ (t, J = 7.8 \text{ Hz, } 1H), \ 2.74 \ (t, J = 7.4 \text{ Hz, } 2H), \ 1.41 \ (s, 18H). \]

\[ ^13C \text{NMR} \ (100 \text{ MHz, CDCl}_3) \delta \ 152.33, \ 147.57, \ 136.93, \ 135.82, \ 134.40, \ 131.32, \ 130.00, \ 129.22, \ 126.73, \ 124.38, \ 122.54, \ 116.48, \ 77.48, \ 77.16, \ 76.84, \ 51.14, \ 40.60, \ 34.53, \ 30.46. \]

HRMS (ESI) cued for C\text{24}H\text{31}BrO (M+H): 415.1631, found: 415.1638.

**Compound 3j**: 4-(1-(4-(benzyloxy)phenyl)but-3-en-1-yl)-2,6-di-tert-butylphenol.

**Compound 3j**: colorless oil, 99% isolated yield.

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \delta \ 7.47 - 7.28 \ (m, 5H), \ 7.15 \ (d, J = 8.6 \text{ Hz, } 2H), \ 7.01 \ (s, 2H), \ 6.90 \ (d, J = 8.6 \text{ Hz, } 2H), \ 5.71 \ (m, J = 17.0, 10.1, 6.8 \text{ Hz, } 1H), \ 5.09 - 4.90 \ (m, 5H), \ 3.87 \ (t, J = 7.9 \text{ Hz, } 1H), \ 2.82 - 2.69 \ (m, 2H), \ 1.40 \ (s, 18H). \]

\[ ^13C \text{NMR} \ (100 \text{ MHz, CDCl}_3) \delta \ 157.12, \ 152.03, \ 137.61, \ 137.58, \ 137.31, \ 135.59, \ 135.56, \ 129.03, \ 128.68, \ 128.03, \ 127.65, \ 124.35, \ 115.97, \ 114.72, \ 70.11, \ 50.58, \ 41.00, \ 34.49, \ 30.48. \]

HRMS (ESI) cued for C\text{31}H\text{38}O\text{2} (M+NH\text{4})^+: 460.3210, found: 460.3219.

**Compound 3k**: 2,6-di-tert-butyl-4-(1-(4-methoxyphenyl)but-3-en-1-yl)phenol.

**Compound 3k**: colorless oil, 99% isolated yield.

\[ ^1H \text{NMR} \ (400 \text{ MHz, CDCl}_3) \delta \ 7.15 \ (d, J = 8.7 \text{ Hz, } 2H), \ 7.01 \ (s, 2H), \ 6.82 \ (d, J = 8.7 \text{ Hz, } 2H), \ 5.80 - 5.63 \ (m, 1H), \ 5.08 - 4.89 \ (m, 3H), \ 3.87 \ (t, J = 7.9 \text{ Hz, } 1H), \ 3.77 \ (s, 3H), \ 2.74 \ (t, J = 7.4 \text{ Hz, } 2H), \ 1.40 \ (s, 18H). \]

\[ ^13C \text{NMR} \ (100 \text{ MHz, CDCl}_3) \delta \ 157.83, \ 152.02, \ 137.62, \ 137.27, \ 135.64, \ 135.56, \ 129.00, \ 124.33, \ 115.95, \ 113.76, \ 55.32, \ 50.56, \ 41.01, \ 34.49, \ 30.48. \]

HRMS (ESI) cued for C\text{25}H\text{34}O\text{2} (M+NH\text{4})^+: 384.2897, found: 384.2897.

**Compound 3l**: 2,6-di-tert-butyl-4-(1-(p-tolyl)but-3-en-1-yl)phenol.
Compound 3l: colorless oil, 99% isolated yield.

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.17 – 7.05 (m, 4H), 7.02 (s, 2H), 5.83 – 5.64 (m, 1H), 5.10 – 4.86 (m, 3H), 3.87 (t, \( J = 7.9 \) Hz, 1H), 2.76 (t, \( J = 7.4 \) Hz, 2H), 2.30 (s, 3H), 1.40 (s, 18H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 152.05, 142.14, 137.64, 135.55, 135.47, 129.13, 127.92, 124.36, 115.93, 51.08, 40.86, 34.49, 30.48, 21.16.

HRMS (ESI) caleld for C\(_{25}\)H\(_{34}\)O (M+NH\(_4\))^+: 368.2948, found: 368.2944.

Compound 3m: 2,6-di-tert-butyl-4-(1-(4-fluorophenyl)but-3-en-1-yl)phenol.

\[ \text{OH} \quad \text{t-Bu} \quad \text{t-Bu} \quad \text{F} \]

Compound 3m: colorless oil, 96% isolated yield.

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.18 (dd, \( J = 8.6, 5.5 \) Hz, 2H), 7.02 – 6.92 (m, 4H), 5.79 – 5.63 (m, 1H), 5.05 (s, 1H), 5.05 – 4.91 (m, 2H), 3.90 (t, \( J = 7.8 \) Hz, 1H), 2.74 (t, \( J = 8.1 \) Hz, 2H), 1.40 (s, 18H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 152.17, 137.23, 135.72, 135.12, 129.54, 129.47, 124.34, 116.27, 115.25, 115.04, 50.56, 40.90, 34.52, 30.47.

HRMS (ESI) caleld for C\(_{24}\)H\(_{31}\)FO (M-H)^-: 353.2286, found: 353.2292.

Compound 3n: 2,6-di-tert-butyl-4-(1-(4-chlorophenyl)but-3-en-1-yl)phenol.

\[ \text{OH} \quad \text{t-Bu} \quad \text{t-Bu} \quad \text{Cl} \]

Compound 3n: colorless oil, 99% isolated yield.

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.24 (d, \( J = 8.0 \) Hz, 2H), 7.16 (d, \( J = 8.2 \) Hz, 2H), 6.99 (s, 2H), 5.83 – 5.61 (m, 1H), 5.06 (s, 1H), 5.05 – 4.92 (m, 2H), 3.89 (t, \( J = 7.8 \) Hz, 1H), 2.74 (t, \( J = 7.4 \) Hz, 2H), 1.40 (s, 18H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 152.24, 143.62, 137.05, 135.75, 134.75, 131.70, 129.50, 128.53, 124.31, 116.40, 50.71, 40.64, 34.51, 30.45.


Compound 3o: 4-(1-(4-bromophenyl)but-3-en-1-yl)-2,6-di-tert-butylphenol.

\[ \text{OH} \quad \text{t-Bu} \quad \text{t-Bu} \]

Compound 3o: 4-(1-(4-bromophenyl)but-3-en-1-yl)-2,6-di-tert-butylphenol.
**Compound 3o**: colorless oil, 92% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 8.3$ Hz, 2H), 6.98 (s, 2H), 5.76 – 5.61 (m, 1H), 5.06 (s, 1H), 5.05 – 4.91 (m, 2H), 3.87 (t, $J = 7.9$ Hz, 1H), 2.74 (t, $J = 7.1$ Hz, 2H), 1.40 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.26, 144.16, 137.01, 135.77, 134.65, 131.47, 129.91, 124.30, 119.81, 116.42, 50.79, 40.56, 34.51, 30.45.

HRMS (ESI) cale for C$_{24}$H$_{31}$BrO (M+H)$^-$: 413.1486, found: 413.1487.

**Compound 3p**: 2,6-di-tert-butyl-4-(1-(4-iodophenyl)but-3-en-1-yl)phenol.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J = 8.3$ Hz, 2H), 7.03 – 6.96 (m, 4H), 5.76 – 5.58 (m, 1H), 5.06 (s, 1H), 5.05 – 4.91 (m, 2H), 3.85 (t, $J = 7.9$ Hz, 1H), 2.79 – 2.68 (m, 2H), 1.40 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.26, 144.89, 137.45, 137.01, 135.77, 134.59, 130.25, 124.29, 116.43, 50.90, 40.48, 34.51, 30.45.

HRMS (ESI) cale for C$_{24}$H$_{31}$IO (M-H)$^-$: 461.1347, found: 461.1343.

**Compound 3q**: 2,6-di-tert-butyl-4-(1-(2,4-dimethylphenyl)but-3-en-1-yl)phenol.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 (d, $J = 7.8$ Hz, 1H), 7.02 – 6.91 (m, 4H), 5.81 – 5.64 (m, 1H), 5.09 – 4.87 (m, 3H), 4.08 (t, $J = 7.8$ Hz, 1H), 2.82 – 2.66 (m, 2H), 2.27 (d, $J = 2.9$ Hz, 6H), 1.38 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.91, 140.03, 137.73, 135.91, 135.45, 135.16, 135.04, 131.30, 126.76, 126.73, 124.62, 115.85, 46.37, 40.91, 34.46, 30.49, 21.05, 20.14.

HRMS (ESI) cale for C$_{26}$H$_{36}$O (M+NH$_4$)$^+$: 382.3104, found: 382.3108.

**Compound 3r**: 2,6-di-tert-butyl-4-(1-(3,4-dimethoxyphenyl)but-3-en-1-yl)phenol.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17 (d, $J = 7.8$ Hz, 2H), 7.02 – 6.91 (m, 4H), 5.81 – 5.64 (m, 1H), 5.09 – 4.87 (m, 3H), 4.08 (t, $J = 7.8$ Hz, 1H), 2.82 – 2.66 (m, 2H), 2.27 (d, $J = 2.9$ Hz, 6H), 1.38 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.91, 140.03, 137.73, 135.91, 135.45, 135.16, 135.04, 131.30, 126.76, 126.73, 124.62, 115.85, 46.37, 40.91, 34.46, 30.49, 21.05, 20.14.

HRMS (ESI) cale for C$_{26}$H$_{36}$O (M+H)$^+$: 382.3104, found: 382.3108.

**Compound 3r**: colorless oil, 99% isolated yield.
\[^{1}\text{H} \text{NMR}\] (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.03 (s, 2H), 6.78 (d, \(J = 7.9\) Hz, 3H), 5.84 – 5.63 (m, 1H), 5.13 – 4.88 (m, 3H), 3.85 (s, 7H), 2.75 (t, \(J = 7.4\) Hz, 2H), 1.40 (s, 18H).

\[^{13}\text{C} \text{NMR}\] (100 MHz, CDCl\textsubscript{3}) \(\delta\) 152.10, 148.83, 147.36, 137.76, 137.58, 135.66, 135.47, 124.33, 120.06, 115.97, 111.66, 111.21, 56.00, 55.94, 53.56, 51.01, 41.17, 34.52, 30.51.

\(\text{HRMS (ESI)}\) caleed for C\textsubscript{26}H\textsubscript{36}O\textsubscript{3} (M+NH\textsubscript{4})\textsuperscript{+}: 414.3003, found: 414.3004.

**Compound 3s:** 2,6-di-tert-butyl-4-(1-(naphthalen-2-yl)but-3-en-1-yl)phenol.

\(\text{Compound 3s: colorless oil, 94% isolated yield.}\)

\[^{1}\text{H} \text{NMR}\] (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.84 – 7.72 (m, 3H), 7.68 (d, \(J = 1.7\) Hz, 1H), 7.49 – 7.33 (m, 3H), 7.08 (s, 2H), 5.84 – 5.68 (m, 1H), 5.15 – 4.86 (m, 3H), 4.08 (t, \(J = 7.8\) Hz, 1H), 2.87 (q, \(J = 7.9, 7.3\) Hz, 2H), 1.40 (s, 18H).

\[^{13}\text{C} \text{NMR}\] (100 MHz, CDCl\textsubscript{3}) \(\delta\) 152.18, 142.65, 137.44, 135.73, 135.12, 133.70, 132.27, 128.02, 127.88, 127.69, 126.92, 126.32, 125.92, 125.35, 124.54, 116.13, 51.52, 40.62, 34.52, 30.50.

\(\text{HRMS (ESI)}\) caleed for C\textsubscript{28}H\textsubscript{34}O (M+NH\textsubscript{4})\textsuperscript{+}: 404.2948, found: 404.2949.

**Compound 3t:** 2,6-dimethyl-4-(1-phenylbut-3-en-1-yl)phenol.

\(\text{Compound 3t: colorless oil, 95% isolated yield.}\)

\[^{1}\text{H} \text{NMR}\] (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.31 – 7.13 (m, 5H), 6.84 (s, 2H), 5.81 – 5.62 (m, 1H), 5.12 – 4.88 (m, 2H), 4.45 (s, 1H), 3.87 (t, \(J = 7.9\) Hz, 1H), 2.81 – 2.72 (m, 2H), 2.20 (s, 6H).

\[^{13}\text{C} \text{NMR}\] (100 MHz, CDCl\textsubscript{3}) \(\delta\) 150.60, 145.21, 137.27, 136.27, 128.49, 128.09, 127.92, 126.14, 122.93, 116.19, 50.65, 40.28, 16.21.

\(\text{HRMS (ESI)}\) caleed for C\textsubscript{18}H\textsubscript{20}O (M+H): 251.1441, found: 251.1446.

**Compound 3u:** 5'-(1-phenylbut-3-en-1-yl)-[1,1':3',1"-terphenyl]-2'-ol.

\(\text{Compound 3u: colorless oil, 96% isolated yield.}\)
H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 7.9 Hz, 4H), 7.48 – 7.40 (m, 4H), 7.40 – 7.33 (m, 2H), 7.27 (d, J = 4.4 Hz, 4H), 7.15 (s, 3H), 5.85 – 5.67 (m, 1H), 5.28 (s, 1H), 5.13 – 4.92 (m, 2H), 4.01 (t, J = 7.9 Hz, 1H), 2.84 (t, J = 7.4 Hz, 2H).

13C NMR (100 MHz, CDCl₃) δ 147.74, 144.80, 137.87, 137.03, 136.83, 129.48, 128.93, 128.68, 128.59, 127.96, 127.71, 126.32, 116.47, 50.79, 40.31.

HRMS (ESI) caleed for C$_{28}$H$_{24}$O (M+NH$_4$)$^+$: 394.2165, found: 394.2173.

**Compound 3v:** 2,6-diisopropyl-4-(1-phenylbut-3-en-1-yl)phenol.

![Image of Compound 3v](image)

**Compound 3v:** colorless oil, 99% isolated yield.

H NMR (400 MHz, CDCl₃) δ 7.30 – 7.20 (m, 4H), 7.16 (t, J = 7.0 Hz, 1H), 6.91 (s, 2H), 5.81 – 5.62 (m, 1H), 5.08 – 4.88 (m, 2H), 4.63 (s, 1H), 3.93 (t, J = 7.9 Hz, 1H), 3.10 (p, J = 6.9 Hz, 2H), 2.82 – 2.74 (m, 2H), 1.23 (dd, J = 6.8, 2.9 Hz, 12H).

13C NMR (100 MHz, CDCl₃) δ 148.38, 145.25, 137.41, 136.38, 133.47, 128.44, 128.01, 126.07, 123.05, 116.11, 51.22, 40.69, 27.46, 22.90.

HRMS (ESI) caleed for C$_{22}$H$_{28}$O (M-H): 307.2067, found: 307.2070.

**Compound 3w:** 2-(tert-butyl)-4-(1-(4-methoxyphenyl)but-3-en-1-yl)-6-methylphenol.

![Image of Compound 3w](image)

**Compound 3w:** colorless oil, 96% isolated yield.

H NMR (400 MHz, CDCl₃) δ 7.14 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 2.2 Hz, 1H), 6.85 – 6.74 (m, 3H), 5.79 – 5.63 (m, 1H), 5.08 – 4.89 (m, 2H), 4.60 (s, 1H), 3.89 – 3.80 (m, 1H), 3.76 (s, 3H), 2.82 – 2.64 (m, 2H), 2.17 (s, 3H), 1.38 (s, 9H).

13C NMR (100 MHz, CDCl₃) δ 164.33, 157.87, 150.96, 137.49, 137.38, 136.22, 135.41, 129.84, 128.88, 127.75, 124.63, 122.92, 116.03, 113.83, 55.33, 50.14, 40.73, 34.68, 29.93, 16.30.

HRMS (ESI) caleed for C$_{22}$H$_{28}$O$_2$ (M+NH$_4$)$^+$: 342.2428, found: 342.3420.

**Compound 3x:** 4-(1-(2-bromophenyl)but-3-en-1-yl)-2-(tert-butyl)-6-methylphenol.

![Image of Compound 3x](image)

**Compound 3x:** 2,6-diisopropyl-4-(1-phenylbut-3-en-1-yl)phenol.
**Compound 3x:** colorless oil, 96% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, $J = 7.7$ Hz, 1H), 7.24 (d, $J = 3.9$ Hz, 2H), 7.10 (d, $J = 2.3$ Hz, 1H), 7.05 – 6.98 (m, 1H), 6.85 (d, $J = 2.4$ Hz, 1H), 5.81 – 5.66 (m, 1H), 5.09 – 4.90 (m, 2H), 4.62 (s, 1H), 4.48 (t, $J = 7.8$ Hz, 1H), 2.84 – 2.71 (m, 2H), 2.19 (s, 3H), 1.39 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.16, 144.20, 136.73, 135.39, 134.21, 133.07, 128.98, 128.11, 127.60, 125.30, 125.22, 122.95, 116.47, 48.73, 40.00, 34.70, 29.93, 16.31.


**Compound 3y:** 2,6-di-tert-butyl-4-(1-(2-(trifluoromethyl)phenyl)but-3-en-1-yl)phenol.

![Compound 3y](image)

**Compound 3y:** colorless oil, 96% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 – 7.58 (m, 1H), 7.49 – 7.38 (m, 2H), 7.25 (d, $J = 5.3$ Hz, 1H), 7.11 (s, 2H), 5.77 – 5.62 (m, 1H), 5.06 (s, 1H), 5.05 – 4.86 (m, 2H), 4.43 (t, $J = 7.8$ Hz, 1H), 3.07 – 2.61 (m, 2H), 1.40 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.24, 144.83, 136.68, 135.59, 133.77, 131.99, 129.64, 125.88, 125.78, 124.69, 116.47, 45.23, 41.13, 34.53, 30.44.

HRMS (ESI) caled for C$_{25}$H$_{31}$F$_3$O (M-H): 403.2254, found: 403.2258.

**Compound 3z:** (E)-4-(1-(4-(benzyloxy)phenyl)-3-phenylallyl)-2,6-di-tert-butylphenol

![Compound 3z](image)

**Compound 3z:** colorless oil, 87% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 – 7.26 (m, 9H), 7.15 (d, $J = 8.5$ Hz, 3H), 7.03 (s, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 6.63 (dd, $J = 15.7$, 7.6 Hz, 1H), 6.33 (d, $J = 15.8$ Hz, 1H), 5.09 (s, 1H), 5.05 (s, 2H), 4.74 (d, $J = 7.6$ Hz, 1H), 1.40 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.33, 152.36, 137.74, 137.27, 136.61, 135.81, 134.26, 133.90, 130.62, 129.70, 128.69, 128.60, 128.05, 127.64, 127.20, 126.41, 125.23, 114.81, 70.17, 53.58, 34.52, 30.47.

HRMS (ESI) caled for C$_{36}$H$_{40}$O$_2$ (M-H): 503.2956, found: 503.2951.

**Compound 4o:** 2-(tert-butyl)-4-(1-(4-chlorophenyl)but-3-en-1-yl)phenol
Compound 4o: colorless oil, 80% isolated yield.

**^1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.24 (d, $J=8.5$ Hz, 2H), 7.14 (d, $J=8.5$ Hz, 2H), 7.09 (d, $J=2.2$ Hz, 1H), 6.87 (dd, $J=8.1$, 2.3 Hz, 1H), 6.57 (d, $J=8.1$ Hz, 1H), 5.81 – 5.58 (m, 1H), 5.14 – 4.89 (m, 2H), 4.64 (s, 1H), 3.91 (t, $J=7.9$ Hz, 1H), 2.82 – 2.66 (m, 2H), 1.37 (s, 9H).

**^13C NMR** (100 MHz, CDCl$_3$) $\delta$ 152.66, 143.59, 136.84, 136.07, 131.82, 129.40, 128.58, 126.89, 125.95, 116.61, 116.54, 50.23, 40.41, 34.71, 29.72.

**HRMS (ESI)** caleed for C$_{20}$H$_{23}$ClO (M-H): 313.1365, found:313.1366.

Compound 5o: 4-(1-(4-chlorophenyl)but-3-en-1-yl)phenol

**^1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.22 (d, $J=8.4$ Hz, 2H), 7.11 (d, $J=8.5$ Hz, 2H), 7.04 (d, $J=8.5$ Hz, 2H), 6.72 (d, $J=8.6$ Hz, 2H), 5.80 – 5.58 (m, 1H), 5.31 (s, 1H), 5.10 – 4.83 (m, 2H), 3.90 (t, $J=7.9$ Hz, 1H), 2.90 – 2.63 (m, 2H).

**^13C NMR** (100 MHz, CDCl$_3$) $\delta$ 153.81, 143.38, 136.57, 136.51, 131.86, 129.31, 129.09, 128.58, 116.70, 115.46, 49.74, 40.08.

**HRMS (ESI)** caleed for C$_{16}$H$_{15}$ClO (M-H): 257.0739, found:257.0744.

Compound 6o: (E)-4,4’-(1,6-bis(4-chlorophenyl)hex-3-ene-1,6-diyl)diphenol

**^1H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.16 (m, 4H), 6.99 (ddd, $J=27.2$, 8.4, 3.5 Hz, 8H), 6.72 (t, $J=9.1$ Hz, 4H), 5.27 (t, $J=3.8$ Hz, 2H), 4.75 (d, $J=10.5$ Hz, 2H), 3.74 (t, $J=7.8$ Hz, 2H), 2.58 (t, $J=6.2$ Hz, 4H).

**^13C NMR** (100 MHz, CDCl$_3$) $\delta$ 153.91, 143.59, 136.44, 131.78, 130.16, 129.29, 129.08, 128.53, 115.39, 50.04, 38.85.

**HRMS (ESI)** caleed for C$_{30}$H$_{26}$Cl$_2$O$_2$ (M-H): 487.1237, found:487.1234.
**Compound 7e**: 4-(1-(2-bromophenyl)-2-(oxiran-2-yl)ethyl)-2,6-di-tert-butylphenol

```
    OH
    t-Bu t-Bu
    Br
```

**Compound 7e**: white solid, 95% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 – 7.51 (m, 1H), 7.34 – 7.27 (m, 1H), 7.24 (d, $J = 3.2$ Hz, 1H), 7.14 – 7.00 (m, 3H), 5.07 (s, 1H), 4.73 – 4.60 (m, 1H), 2.94 – 2.81 (m, 1H), 2.67 (dt, $J = 8.3$, 4.5 Hz, 1H), 2.48 – 2.25 (m, 2H), 2.22 – 2.05 (m, 1H), 1.40 (d, $J = 2.0$ Hz, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.00, 135.84, 133.50, 133.18, 128.86, 128.68, 127.80, 124.67, 124.45, 51.14, 47.88, 46.40, 38.92, 34.52, 30.46.

HRMS (ESI) caled for C$_{24}$H$_{31}$BrO$_2$: 430.1435, found: 429.1444.

**Compound 4n**: 2,6-di-tert-butyl-4-(1-(4-chlorophenyl)-4-hydroxybutyl)phenol

```
    OH
    t-Bu t-Bu
    Cl
```

**Compound 4n**: white oil, 88% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 (d, $J = 8.7$ Hz, 2H), 7.17 (d, $J = 8.5$ Hz, 2H), 6.98 (s, 2H), 5.05 (s, 1H), 3.78 (t, $J = 7.8$ Hz, 1H), 3.63 (q, $J = 6.0$ Hz, 2H), 2.04 (q, $J = 7.8$ Hz, 2H), 1.57 – 1.45 (m, 3H), 1.40 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.23, 144.11, 135.85, 135.16, 131.70, 129.32, 128.60, 124.15, 63.01, 50.75, 34.51, 32.49, 31.49, 30.47.

HRMS (ESI) caled for C$_{24}$H$_{33}$ClO$_2$ (M+NH$_4$)$^+$: 406.2507, found: 406.2515.

**Compound 5n**: 4-(4-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)butanal

```
    OH
    t-Bu t-Bu
```

**Compound 5n**: white oil, 97% isolated yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.71 (t, $J = 1.3$ Hz, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.5$ Hz, 2H), 6.97 (s, 2H), 5.09 (s, 1H), 3.79 (t, $J = 7.8$ Hz, 1H), 2.44 – 2.36 (m, 2H), 2.34 – 2.26 (m, 2H), 1.40 (s, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.09, 152.45, 143.23, 136.02, 134.12, 132.02, 129.25, 128.74, 124.17, 49.97, 42.65, 34.49, 30.42, 28.32.
HRMS (ESI) caled for C$_{24}$H$_{31}$ClO$_2$ (M+H)$^+_	ext{+}$: 387.2085, found:387.2089.

**Compound 6n**: 4-(4-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)butanoic acid

- **Compound 6n**: white solid, 76% isolated yield.
- $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 (d, $J = 2.4$ Hz, 2H), 7.22 – 7.12 (m, 2H), 6.97 (d, $J = 2.3$ Hz, 2H), 5.08 (s, 1H), 3.82 (d, $J = 7.3$ Hz, 1H), 2.30 (d, $J = 4.1$ Hz, 4H), 1.39 (d, $J = 2.3$ Hz, 18H).
- $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 179.76, 152.44, 143.16, 135.98, 134.07, 132.02, 129.31, 128.73, 124.20, 49.98, 34.50, 32.68, 30.90, 30.42.
- HRMS (ESI) caled for C$_{24}$H$_{31}$ClO$_2$ (M+NH$_4^+$): 420.2300, found:420.2298.

**Compound 7n**: (E)-4-(4-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)butanal oxime

- **Compound 7n**: white oil, 80% isolated yield.
- $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J = 5.5$ Hz, 1H), 7.29 – 7.12 (m, 4H), 6.97 (d, $J = 4.6$ Hz, 2H), 5.07 (s, 1H), 3.89 – 3.72 (m, 1H), 2.42 – 2.26 (m, 1H), 2.26 – 2.09 (m, 3H), 1.40 (d, $J = 1.5$ Hz, 18H).
- $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.38, 151.77, 143.36, 135.95, 134.43, 131.93, 129.30, 128.72, 124.16, 50.17, 34.50, 32.85, 30.44, 28.22.
- HRMS (ESI) caled for C$_{24}$H$_{32}$ClNO$_2$ (M+H)$^+_	ext{+}$: 402.2194, found: 402.2192.

**Compound 8n**: (E)-2,6-di-tert-butyl-4-(1-(4-chlorophenyl)-4-(2-(2,4-dinitrophenyl)hydrazono)butyl)phenol

- **Compound 8n**: yellow solid, 90% isolated yield.
- $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.97 (s, 1H), 9.09 (d, $J = 2.6$ Hz, 1H), 8.27 (dd, $J = 9.5$, 2.6 Hz, 1H), 7.88 (d, $J = 9.6$ Hz, 1H), 7.49 (t, $J = 4.9$ Hz, 1H), 7.30 – 7.19 (m, 4H), 7.02 (s, 2H), 5.11 (s, 1H), 3.88 (t, $J = 7.6$ Hz, 1H), 2.49 – 2.27 (m, 4H), 1.41 (s, 18H).
- $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.45, 152.07, 145.12, 143.25, 137.84, 136.06, 134.24, 132.04,
130.02, 129.27, 128.84, 128.75, 124.14, 123.58, 116.56, 50.32, 34.50, 32.64, 31.32, 30.41.

**HRMS (ESI)** caled for C$_{30}$H$_{35}$ClN$_4$O$_3$ (M+H)$^+$: 567.2369, found:567.2356.
6. NMR copies

3a $^1$H NMR, 400MHz, CDCl$_3$

3a $^{13}$C NMR, 100MHz, CDCl$_3$
$^{1}H$ NMR, 400MHz, CDCl$_3$

3b $^{1}H$ NMR, 400MHz, CDCl$_3$
$^1$H NMR, 400MHz, CDCl$_3$

3c

$^1$C NMR, 100MHz, CDCl$_3$
$3^d$ $^1H$ NMR, 400MHz, CDCl$_3$

$3^d$ $^{13}$C NMR, 100MHz, CDCl$_3$
$^{1}H$ NMR, 400MHz, CDCl$_3$

$^{13}C$ NMR, 100MHz, CDCl$_3$
$3f$ $^1$H NMR, 400MHz, CDCl$_3$

$3f$ $^{13}$C NMR, 100MHz, CDCl$_3$
$3g$ $^1H$ NMR, 400MHz, CDCl$_3$

$3g$ $^{13}C$ NMR, 100MHz, CDCl$_3$
$3^1$H NMR, 400MHz, CDCl$_3$

$3^1$C NMR, 100MHz, CDCl$_3$
$^1$H NMR, 400MHz, CDCl$_3$

$^1$C NMR, 100MHz, CDCl$_3$
3j $^1$H NMR, 400MHz, CDCl$_3$

3j $^{13}$C NMR, 100MHz, CDCl$_3$
$^1$H NMR, 400MHz, CDCl$_3$

$^1$C NMR, 100MHz, CDCl$_3$
$^{13}$C NMR, 100MHz, CDCl$_3$

$^1$H NMR, 400MHz, CDCl$_3$
$3m \text{ }^1\text{H NMR, 400MHz, CDCl}_3$
$3n^{1}H$ NMR, 400MHz, CDCl$_3$

$3n^{13}C$ NMR, 100MHz, CDCl$_3$
$\textbf{3o}^{1}H$ NMR, 400MHz, CDCl$_3$

$\textbf{3o}^{13}C$ NMR, 100MHz, CDCl$_3$
$\text{H NMR, 400MHz, CDCl}_3$

$\text{C NMR, 100MHz, CDCl}_3$
$^1$H NMR, 400MHz, CDCl$_3$

$^13$C NMR, 100MHz, CDCl$_3$
3r \(^1\)H NMR, 400MHz, CDCl\(_3\)

3r \(^{13}\)C NMR, 100MHz, CDCl\(_3\)
$^{1}H$ NMR, 400MHz, CDCl$_3$  

$^{13}C$ NMR, 100MHz, CDCl$_3$
3t $^1$H NMR, 400MHz, CDCl$_3$

3t $^{13}$C NMR, 100MHz, CDCl$_3$
$^1$H NMR, 400MHz, CDCl$_3$

$^{13}$C NMR, 100MHz, CDCl$_3$
$^1$H NMR, 400MHz, CDCl₃

$^{13}$C NMR, 100MHz, CDCl₃
$3w$ $^1$H NMR, 400MHz, CDCl$_3$

$3w$ $^{13}$C NMR, 100MHz, CDCl$_3$
$^1$H NMR, 400MHz, CDCl$_3$

$^1$C NMR, 100MHz, CDCl$_3$
$3^y$C NMR, 100MHz, CDCl₃

$3^y$H NMR, 400MHz, CDCl₃
$^1$H NMR, 400MHz, CDCl$_3$

$^13$C NMR, 100MHz, CDCl$_3$
50^1H NMR, 400MHz, CDCl$_3$

50^13C NMR, 100MHz, CDCl$_3$
$^1$H NMR, 400MHz, CDCl$_3$

$^{13}$C NMR, 100MHz, CDCl$_3$
$7e^1$H NMR, 400MHz, CDCl$_3$

$7e^{13}$C NMR, 100MHz, CDCl$_3$
$^1H$ NMR, 400MHz, CDCl$_3$

$^{13}C$ NMR, 100MHz, CDCl$_3$
$^{1}H$ NMR, 400MHz, CDCl$_3$

$^{13}C$ NMR, 100MHz, CDCl$_3$
$^1$H NMR, 400MHz, CDCl$_3$

$^{13}$C NMR, 100MHz, CDCl$_3$
\[ \text{\( ^1H \) NMR, 400MHz, CDCl}_3 \]

\[ \text{\( ^13C \) NMR, 100MHz, CDCl}_3 \]
7. X-ray crystallography data of 6n

Table 1 Crystal data and structure refinement for CCDC 1521335

<table>
<thead>
<tr>
<th>Identification code</th>
<th>CCDC 1521335</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C24 H31 Cl O3</td>
</tr>
<tr>
<td>Formula weight</td>
<td>402.94</td>
</tr>
<tr>
<td>Temperature</td>
<td>113(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2(1)/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 10.500(4) Å, alpha = 90 deg.</td>
</tr>
<tr>
<td></td>
<td>b = 9.336(4) Å, beta = 100.864(9) deg.</td>
</tr>
<tr>
<td></td>
<td>c = 22.910(10) Å, gamma = 90 deg.</td>
</tr>
<tr>
<td>Volume</td>
<td>2205.7(15) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.213 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.194 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>864</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.18 x 0.12 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.19 to 25.02 deg.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-12&lt;=h&lt;=12, -11&lt;=k&lt;=10, -27&lt;=l&lt;=27</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>17912 / 3869 [R(int) = 0.1143]</td>
</tr>
<tr>
<td>Completeness to theta = 25.02</td>
<td>99.6 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9771 and 0.9622</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
</tbody>
</table>

Figure 1 X-ray crystallography data of 6n.
Data / restraints / parameters 3869 / 106 / 270
Goodness-of-fit on F^2 1.002
Final R indices [I>2sigma(I)] R1 = 0.0799, wR2 = 0.2117
R indices (all data) R1 = 0.1257, wR2 = 0.2432
Largest diff. peak and hole 0.634 and -0.365 e.A^-3
8. Reference


